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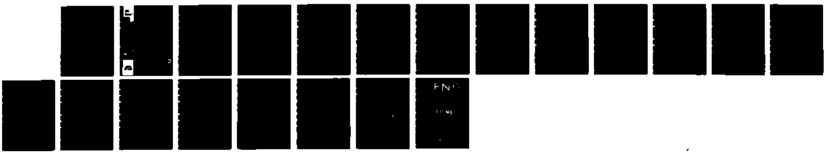

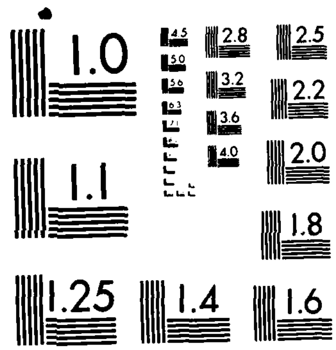

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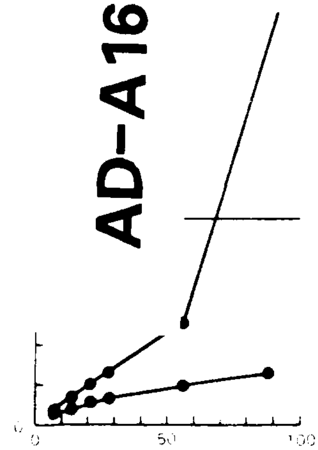

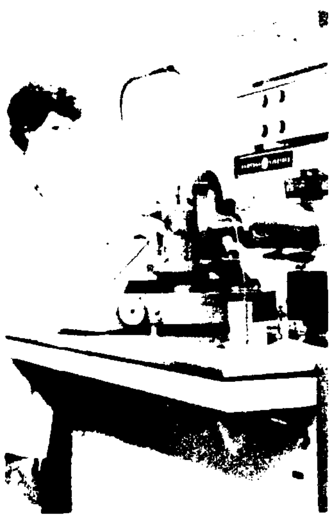

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MISCELLANEOUS PAPER SL-85-14

SULFATE RESISTANCE OF HYDRAULIC CEMENTS CONTAINING BLAST-FURNACE SLAG

by

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Structures Laboratory

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US ARMY ENGINEER WATERWAYS EXPERIMENT STATION

September 1985

Final Report

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Recent research at the US Army Engineer Waterways Experiment Station (WES) has included two projects having the objective of developing a test for sulfate resistance. This work included tests using one portland blast-furnace slag cement from Alabama, one from Michigan, one from Pennsylvania, and two from Germany. In addition, samples of the comparable Type I from the plant in Alabama, slag used for the Michigan IS, and a Type V cement from Canada were included. Finally, tests were made using a natural pozzolan from California

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20. ABSTRACT (Continued).

as 30 percent replacement by solid volume for the two cements from Alabama and the one from Canada.

Expansion testing for sulfate resistance was usually in a 5 percent solution of sodium sulfate. Other tests included materials analysis before use and X-ray diffraction examination of mortar-bar paste concentrations after the expansion tests, periodic determinations of relative modulus of elasticity of mortar bars, and partial chemical analyses of the test solution before and during the expansion testing.

The report concentrates on expansion data and materials characterization and efforts to relate these factors.

In general, specimens made using the cements containing slag showed more than 0.1 percent expansion in the mortar-bar test. The addition of natural pozzolan reduced the expansion.

Preface

This report was presented at a workshop on "Slag Cements: Research and Practice" held at Pennsylvania State University on 12-14 March 1984. The results included were part of those of a larger research project, CWIS Work Unit No. 31295, "Sulfate Resistance of Portland and Portland-Pozzolan Cements," sponsored by the Office, Chief of Engineers, US Army, and an American Society for Testing and Materials (ASTM) cooperative interlaboratory test program. All of the work was performed in the Concrete Technology Division (CTD) of the Structures Laboratory (SL), US Army Engineer Waterways Experiment Station (WES), under the direction of Mr. John M. Scanlon, Chief, CTD, and Mr. Bryant Mather, Chief, SL. Mrs. K. Mather was project leader for both projects. Mr. A. D. Buck, CTD, prepared the report.

The Concrete Technology Information Analysis Center (CTIAC) provided funds to publish this report, which is CTIAC report No. 72.

The Commander and Director of WES during the preparation of this report was COL Robert C. Lee, CE; Technical Director was Mr. F. R. Brown. During the publication of this report, COL Allen F. Grum, USA, was Director of WES; Dr. Robert W. Whalin was Technical Director.

Contents

Conversion Factors, Non-SI to SI (Metric) Units of Measurement

Non-SI units of measurement used in this report can be converted to SI (metric) units as follows:

Multiply	By	To Obtain
Fahrenheit degrees	5/9	Celsius degrees or Kelvins*
pounds (force) per square inch	6.894757	kilopascals

* To obtain Celsius (C) temperature readings from Fahrenheit (F) readings, use the following formula: C = (5/9)(F - 32). To obtain Kelvin (K) readings, use: K = (5/9)(F - 32) + 273.15.

SULFATE RESISTANCE OF HYDRAULIC CEMENTS CONTAINING BLAST-FURNACE SLAG

Introduction

1. As part of one US Army Corps of Engineers research program and one American Society for Testing and Materials (ASTM) cooperative program performed in the Concrete Technology Division of the Structures Laboratory of the US Army Engineer Waterways Experiment Station (WES) in the 1970's, five portland blast-furnace slag cements were tested for sulfate resistance. The major intent of this program was to develop a new standardized test for determining sulfate resistance that would be more applicable for testing blended cements than ASTM C 452. The test now exists; it is ASTM C 1012-84. That work included characterization of materials, periodic expansion measurements, periodic determinations of relative modulus of elasticity (E), periodic chemical analysis of test solutions, and examination of the paste portion of mortar bars by X-ray diffraction (XRD) after expansion testing. This report concentrates on expansion results, posttest examination by XRD, and materials characteristics.

Materials

2. The following samples were included in the work:

   a. Three Type IS cements: Alabama (RC-752), Michigan (RC-758), and Pennsylvania (RC-833).

   b. The Type I portland cement from Alabama (RC-751) ground from similar clinker to that used with slag to make RC-752.

   c. The granulated blast-furnace slag from Michigan (AD-537) combined with portland cement clinker to make Type IS RC-758.

   d. A German Hochofen cement (USCEC-1C-1). (Hochofenzement must now contain between 41 and 85 percent blast-furnace slag.)

   e. A German Eisenportland cement (USCEC-1C-2). (Eisenportlandzement may not contain over 40 percent blast-furnace slag.)

   f. A Type V portland cement from Canada (RC-755).

   g. A natural pozzolan from California (AD-518). This was used as a 30 percent solid volume replacement for the Type V and the two cements (I, IS) from Alabama.

h. Graded-standard sand, meeting ASTM C 778, was used to make mortar bars.

Test Procedure

3. Sets of mortar bars and cubes were made, subjected to accelerated curing at about 100° F* for about 24 hours, and then placed in storage at ambient temperature. Compressive strength development was monitored by periodic tests of cubes. For all of the mixtures described herein except for the IS cement from Pennsylvania (RC-833), expansion testing of the mortar bars was started when compressive strength was expected to be about 4,000 psi; testing was started at about 3,000 psi for the Pennsylvania IS cement mixture.

4. Mortars with portland cement were made with a water-cement ratio of 0.485; those of the IS cements or cements with natural pozzolan were made to have a flow of 107 ± 10 and water was adjusted as necessary.

5. Mortar bars were immersed in 5 percent sodium sulfate solution (0.352 M) at about 74° F and tested periodically for 1 year unless failure, defined as expansion greater than 0.1 percent, occurred first. The Pennsylvania Type IS cement was part of the ASTM cooperative testing; it was tested in the sodium sulfate solution and in a mixed solution containing both sodium sulfate and magnesium sulfate, each at 0.176 M. A cement paste concentrate was prepared from one mortar bar of each set after expansion testing was stopped; this paste was examined by XRD. In addition, all of the cements, the natural pozzolan, and the slag were examined by XRD. XRD patterns were used to estimate amounts of C_3A**, types of C_3A, and composition of the aluminoferrite phase.

Results

6. None of the five slag-bearing cements provided effective sulfate resistance. As shown in Table 1, mortar bar sets expanded from 0.1 to 1.3 percent during periods that extended to 1 year. Table 1 also shows the

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* A table of factors for converting non-SI units of measurements to SI (metric) units is presented on page 3.

** Usual cement notation where C is CaO, A is Al_2O_3, and F is Fe_2O_3.

approximate times required for the expansion to reach the 0.1 percent level; these times were from approximately 50 to 300 days. While not usually specified, slag levels were judged to be lower than needed for effective sulfate resistance (Gutt and Harrison 1977). Figure 1 shows the expansion curves for the two IS cements (RC-758, RC-833) from Michigan and Pennsylvania and Figure 2 shows expansion curves for the two German cements.

7. Table 2 shows the effects of added natural pozzolan in reducing expansion due to sulfate attack. This comparison includes the Type V cement from Canada (RC-755), the Alabama Type I cement (RC-751), and the matching Type IS cement (RC-752). Figure 3 graphically compares the effect of the pozzolan on the portland cement compared to the effect of slag on the same cement. The presence of approximately 25 percent slag reduced expansion from 1.04 percent at 146 days to 0.08 percent at 292 days, while 30 percent pozzolan reduced the 1.04 percent to 0.05 percent at 365 days. As Table 2 shows, the use of the pozzolan always reduced expansion by 50 percent or more for each of the three cements.

8. Table 3 repeats the expansion data and presents information about the C_3A and type of aluminoferrite in the five slag-bearing cements that were tested.

9. Table 4 deals with hydration products as determined by XRD. As shown, 10 different samples were examined and results were more similar than different. Ettringite, calcium hydroxide (CH), and gypsum were usually found and generally in similar amounts when no natural pozzolan was included. The significant exception to this was the presence of tetracalcium aluminate monosulfate-12-hydrate (monosulfoaluminate) in the Hochofen cement paste concentration. Its presence was probably due to lack of sulfate (as gypsum) although the reason for this is not obvious. As expected, the presence of the natural pozzolan reduced the amounts of CH and gypsum and had no significant effect on ettringite levels. The amount of ettringite did not change with expansion levels nor were any other significant compositional changes apparent.

10. The granulated blast-furnace slag (AD-537) used in the IS cement from Michigan was found by XRD to be largely glassy with minor amounts of metallic iron, calcite, monticellite, akermanite, and merwinite. The natural pozzolan was about 80 percent volcanic glass with some quartz and feldspars, and smaller amounts of cristobalite, hematite, magnetite, biotite, and gypsum. It probably contained less glass than the granulated slag.

Discussion

11. Actual slag content was known only for the Pennsylvania IS cement (36 percent), but was believed to be fairly low for the other four cements. This was based on the fact that the addition of a glassy material, such as slag to cement, increases the background and lowers peak heights of the mixture, as seen by XRD (WES 1956). Comparison of XRD patterns for the Alabama cements with and without slag and of the other XRD patterns showed generally similar background levels. This was taken to indicate that slag levels were generally low. Solubility data for these materials in maleic acid indicated the Hochofen cement had more residue and thus more slag than the other four slag-bearing cements. It was indicated almost 20 years ago (WES 1956) that no generally acceptable method for determining slag content of a slag-bearing cement was known. This is probably still true.

12. There is a relation between C_3A content of portland cement and expansion due to sulfate attack, but other factors influence the performance (ASTM 1956; McMillan, et al. 1949). This was shown by Mather (B. Mather 1965). It was determined that two portland cements of high and about equal C_3A contents (calculated from chemical analysis) had much different C_3A contents, as indicated by XRD; each caused excessive expansions, but at different rates. At that time, it was judged that the one with some C_3A in the form of "glass" was more sulfate resistant. This concept was in agreement with Bogue (1949).

13. Since efforts in 1965 to correlate mortar bar expansion resulting from sulfate resistance testing with amounts of C_3A determined by XRD were not too successful (B. Mather 1965), an evaluation of the results led to the recommendation that future efforts include determination of type of C_3A and type of aluminoferrite. Thus, the present study included determination of type of C_3A (Burkes and Buck 1983) and type of aluminoferrite as well as relative amounts of C_3A. As can be seen in Table 3, amount of expansion did not correlate with amount of C_3A since the two cements (RC-752, RC-758) determined (by XRD) to have the most C_3A, had the most (1.3 percent) and the least (0.1 percent) expansion in mortar bars. All of the aluminoferrites were found to be C_4AF or C_6AF_2 or had compositions between these two adjacent phases so that no clear relationship between aluminoferrite composition and expansion is obvious (Table 3). There did seem to be a definte difference in type of C_3A for the

two cements with the most C_3A. RC-752 has cubic C_3A while RC-758 has mixed forms which include cubic C_3A. This difference in C_3A type could explain some of the large differences in expansion between these two cements if the cubic form was less reactive. However, this would be directly opposite of what Regourd et al. (1973) found in their work. The present data are too few to claim that a difference in form of C_3A was significant. Related data were discussed by Mather (K. Mather 1980).

14. Determination of hydrated phases by XRD after testing for sulfate resistance did not prove to be very helpful in ranking cements by potential sulfate resistance.

15. None of the five slag-bearing cements would be considered adequately sulfate resistant since mortar bars made with them had expansions ranging from 0.1 to 1.3 percent by 1 year with 0.1 defined as failure in this work. This is not surprising since C_3A contents were generally high, although not specifically known, and slag contents were probably low. In general, high slag contents ($\geq$65 percent) are required for satisfactory sulfate resistance of slag cements (Gutt and Harrison 1977).

Conclusions

16. Expansion testing of five slag-bearing cements by immersion of mortar bars in a 5 percent solution of sodium sulfate solution showed that none kept expansion below 0.1 percent for periods up to 1 year.

17. Addition of 30 percent natural pozzolan by solid volume to Type V cement, to Type I cement, and to its companion Type IS cement resulted in reductions of expansions of at least 50 percent in each case. The combination of this pozzolan with the Type I cement was more effective in reducing expansion than addition of an estimated 25 percent slag to the same Type I cement.

18. Efforts to correlate relative C_3A contents, C_3A types, aluminoferrite composition, hydration products of the cements after expansion testing, or combinations of these failed to provide a satisfactory basis for prediction of the expansion levels that were obtained by testing.

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Table 1

Slag Contents and Expansion Data for Three Type IS Slag Cements, One Eisenportland, and One Hochofen Type Slag Cement

		Expansion in 5% Na_2SO_4 Solution, %	
Cement Identification	Slag Content, %	Time to 0.1 days	Total and Duration days
RC-752 (Alabama)	~25 (Estimated)	~300	0.1 (292)
RC-758 (Michigan)	~25 (Estimated)	50	1.3 (120)
RC-833 (Pennsylvania)	36	200	0.3 (365)*
Eisenportland	≤35	230	1.3 (365)
Hochofen	36** to 85†	200	0.5 (365)

* Expansion was 0.5 percent at 365 days in mixed solution of sodium and magnesium silfate.

** Information supplied with cement sample; specification information says 41 to 85.

† Probably less than 50 percent.

Table 2

Effect of Addition of Natural Pozzolan* on Expansion in 5 Percent Sodium Sulfate Solution

Cement Identification	Total Expansion, %, and Duration of Test (days)
Type V RC-755	0.06 (365)
RC-755 and Natural Pozzolan	0.03 (365)
Type I RC-751	1.04 (146)
RC-751 and Natural Pozzolan	0.05 (365)
Type IS RC-752	0.08 (292)
RC-752 and Natural Pozzolan	0.04 (365)

* 30 percent by solid volume.

Table 3

C_3A, Aluminoferrite, and Expansion Data

for Five Slag-Bearing Cements

Cement	C_3A Calculated %	C_3A XRD Ranking	C_3A Type	AF* Type	Total Expansion
RC-752 (Alabama)	~8	Most and about equal	Cubic	Between C_4AF and C_6AF_2	0.1
RC-758 (Michigan)	~9		Mixed	C_6AF_2	1.3
RC-833 (Pennsylvania)	Unknown	Third	Mixed	C_6AF_2	0.3
Eisenportland	Unknown	Fourth	Mixed**	C_4AF	1.3
Hochofen	Unknown	Least	Cubic**	Between C_4AF and C_6AF_2	0.5

* Type of aluminoferrite based on position of the (141) peak in XRD patterns.

** Tentative determination due to smaller amounts of C_3A and decreased peak intensities.

Table 4

Hydration Products Identified by XRD After Expansion Testing in 5 Percent Sodium Sulfate Solution

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Samples

Type I RC-755 cement (Canada), same with natural pozzolan

Type I RC-751 cement (Alabama), same with natural pozzolan

Type IS RC-752 cement (Alabama), same with natural pozzolan

Type IS RC-758 cement (Michigan)

Type IS RC-833 cement (Pennsylvania)

Eisenportland cement

Hochofen cement

Hydration Products*

Ettringite, Calcium Hydroxide (CH), Gypsum

Observations

1. Effect of natural pozzolan.
   a. Ettringite (E) - no effect.
   b. Less calcium hydroxide (CH).
   c. Less gypsum (G).
2. Much less gypsum in Hochofen paste than in pastes of other cements (no pozzolan) and monosulfoaluminate was present.
3. Without natural pozzolan, amounts of E, CH, and G generally similar except that less E in Type V cement paste.

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* Samples were cement paste concentrations from mortar bars.

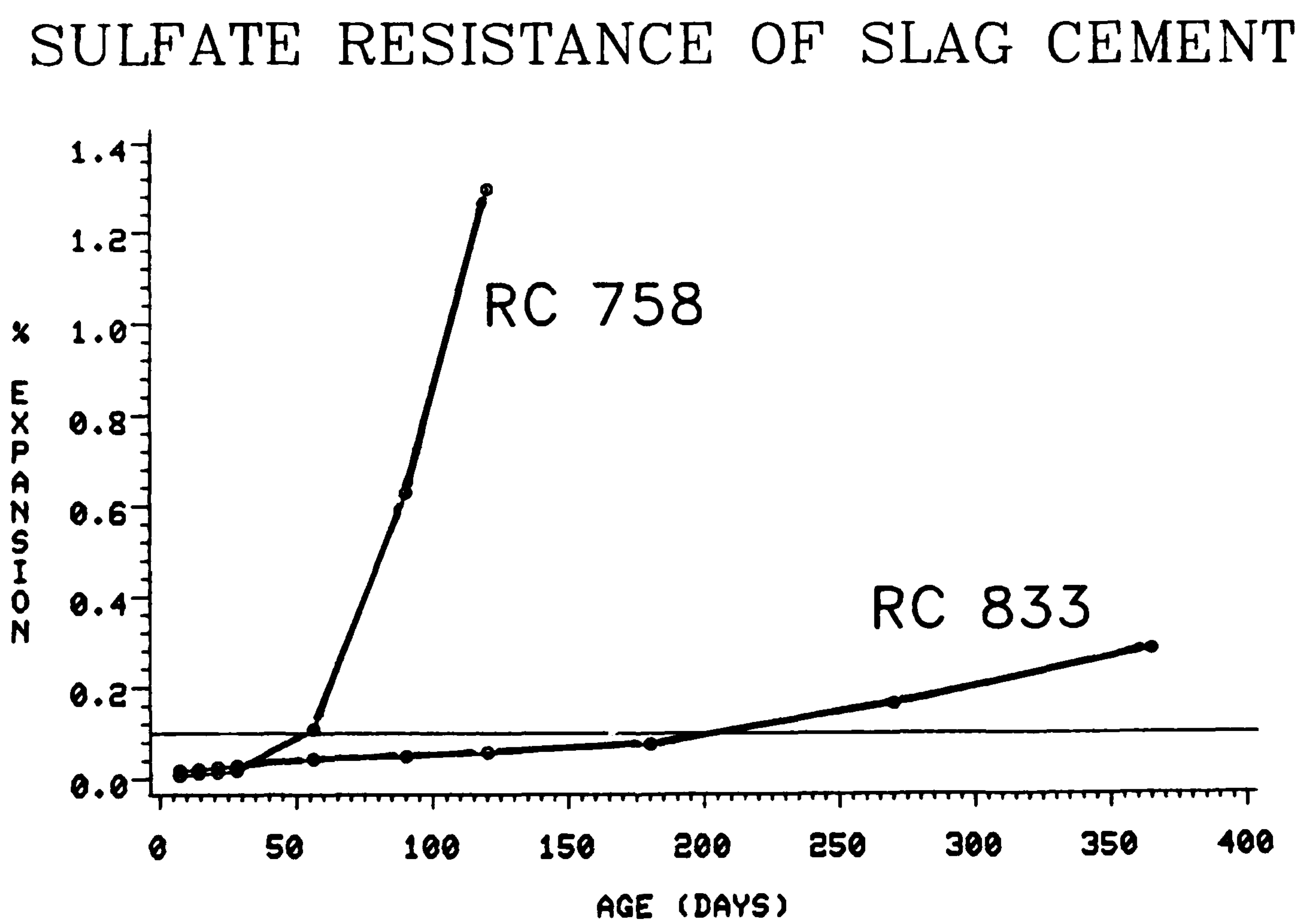

Figure 1. Expansion curves for the Michigan and Pennsylvania IS cements

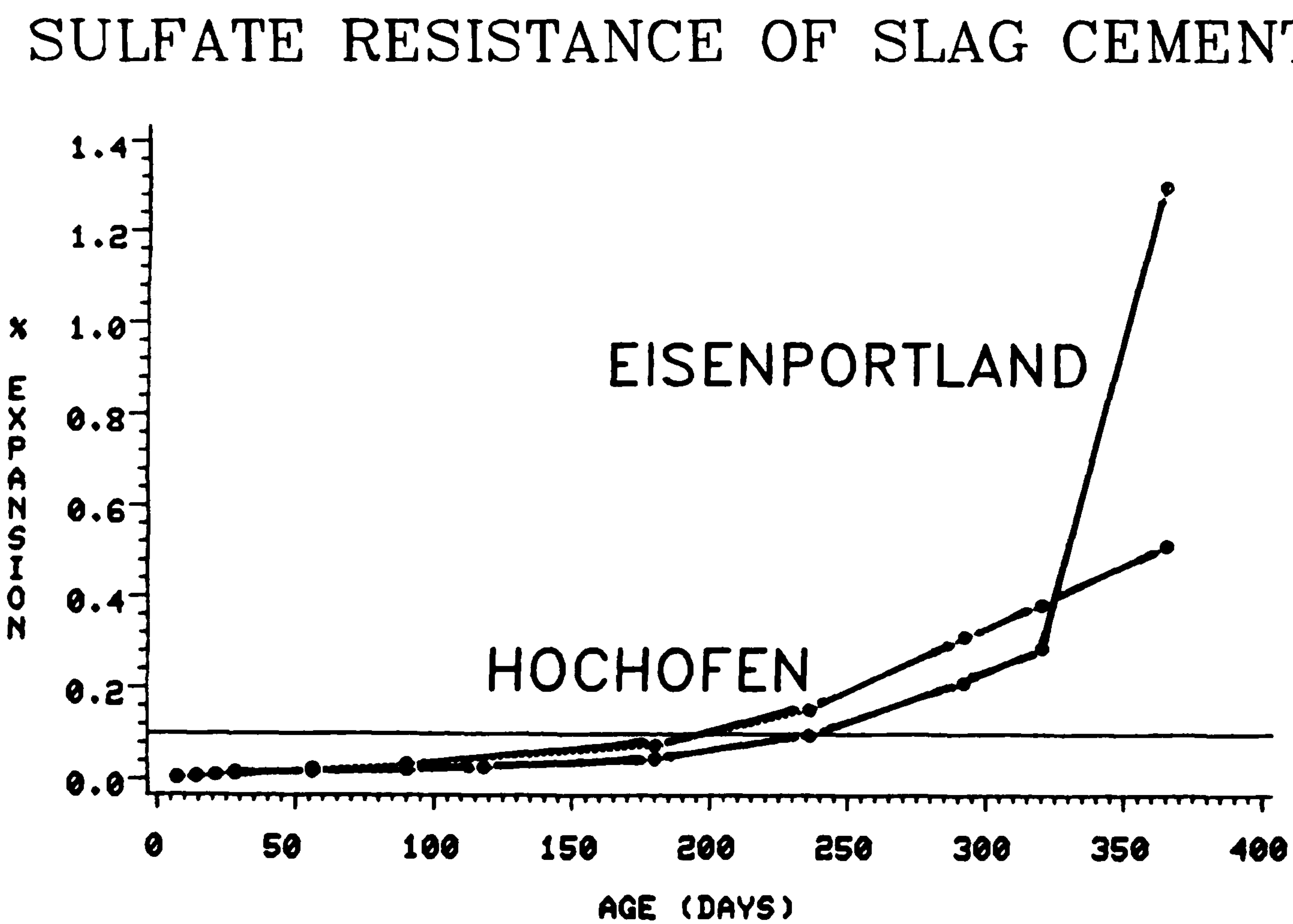

Figure 2. Expansion curves for the two German cements

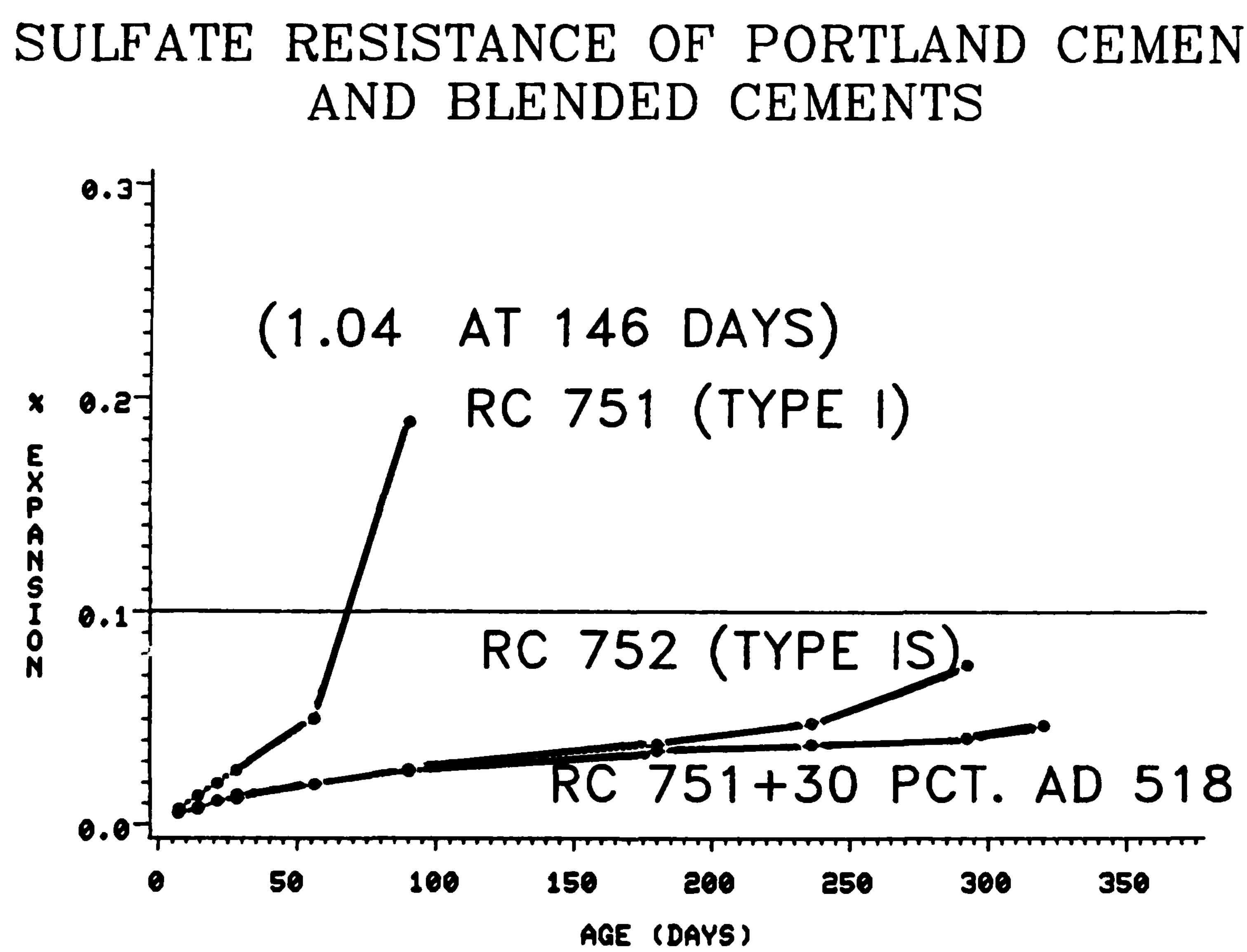

Figure 3. Effect of pozzolan versus effect of slag on portland cement

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